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Name of invention: optical phosphate glass
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Publicized Report of Patent

Detailed Report

1. Name of invention

Optical phosphate glass

2. Sphere of the patent application

(Claim 1)

Claim 1 is concerning an optical phosphate glass which consists of the following composition by weight %. The amount of Ti, Cr, Ma, Fe, Co, Ni is 5 ppm or less of the total. Its optical constants are within the range defined by the following seven points: point A (1.60, 69), point B (1.62, 64), point C (1.62, 47), point D (1.55, 50), point E (1.50, 68), point F (1.50, 73), and point G (1.56, 73) as shown in figure 1.

Note

P_2O_5	20 to 75 %
$Al_2O_3 + B_2O_2$	0.5 to 20 %
R_2O (R is Li, Ma, K)	0 to 14 %
RO (R is Mg, Ca, Sr, Ba, Pb)	1 to 60 %
F	0 to 20 %

(Claim 2)

Claim 2 is regarding the optical phosphate glass stated in claim 1 where the ratio of P_2O_5 and F is as follows.

Note

P_2O_5	60 to 75 %
F	0.1 to 10 %

(Claim 3)

Claim 3 is regarding the optical phosphate glass in claim 1 where the amount of P_2O_5 is as follows.

P_2O_5	20 to 60 %

(Claim 4)

Claim 4 is regarding the optical phosphate glass in claim 1 where the ratio of P_2O_5 and PbO is as follows.

P_2O_5	50 to 75 %
PbO	5 to 35 %

3. Detailed explanation of this invention

(Field of industrial use)

This invention is regarding an optical phosphate glass which has extremely high transmissivity for UV.

(Prior art)

Optical designers have demanded optical glass with various optical constants such as refractive index n_d and dispersion index (Abbe's number ν_d).

(Problems that this invention tries to solve)

Recently, advanced techniques have reached optical glass also. The previous interest in visible light has been replaced by interest in UV transmission with short wavelength.

For instance, an optical glass which has optical constants within the range defined by the following seven points; point A (1.60, 69), point B (1.62, 64), point C (1.62, 47), point D (1.55, 50), point E (1.50, 68), point F (1.50, 73), and point G (1.56, 73) shown in the attached figure 1 (n_d, ν_d) with high UV transmissivity is demanded.

However, former glass with optical constants within this range has low transmissivity for UV, and it has not been satisfactory.

When a lens is manufactured using glass with low transmissivity, UV energy is absorbed inside the lens and is transformed into heat. Then temperature increases and the lens expands. As a result, original optical performance changes.

Accordingly, the object of this invention is to offer optical glass with high transmissivity for UV within the range of the above optical constants.

(Steps for solution)

The inventor of this invention made thorough research on this matter. The following facts were found as a result. Optical glass which has a composition selected from the range stated below and which also contains less than 5 ppm of the following impurities - Ti, Cr, Ma, Fe, Co, Mi and Cu – meets these requirements. Not only that, it is less dependent on melting conditions, and it has sufficient chemical resistance. These findings led to the completion of this invention.

Accordingly, this invention offers an optical phosphate glass with the following composition in weight %. The amount of Ti, Cr, Ma, Fe, Co, and Ni is 5 ppm or less of the total. It also has optical constants within the range defined by the following seven points: point A (1.60, 69), point B (1.62, 64), point C (1.62, 47), point D (1.55, 50), point E (1.50, 68), point F (1.50, 73), and point G (1.56, 73) as shown in the figure 1.

P_2O_5	20 to 75 %
$Al_2O_3 + B_2O_2$	0.5 to 20 %
R_2O (R is Li, Ma, K)	0 to 14 %
RO (R is Mg, Ca, Sr, Ba, Pb)	1 to 60 %
F	0 to 20 %

(Function)

The basic components of the glass in this invention are P_2O5-Al_2O_3-RO. Fluorine is introduced ad required to improve melting and stabilization. The reasons that the composition range of each component is restricted as stated above follow.

P_2O_5 makes the structure of the glass of this invention. Among glass forming oxides, its short wavelength absorbance is lowest such as 145 nm (SiO_2 is 162 nm, BsO_2 is 200 nm). Because of this, it is best for high UV rays transmission even when other decorative oxide or colored impurities are present. However, it is harder to form than SiO_2, B_2O_3. Also, it is prone to lose transmittance and is inferior in chemical resistance. If it is less than 20 %, it not only becomes susceptible to losing transmittance, its short wavelength transmitting performance is also lowered. On the other hand, if it exceeds 75 %, its chemical resistance is poor, and it will not be practical for actual use. Al_2O_3, B_2O_2 are both trihydric cations. Among pentahydric glass phosphates, it forms part of a square structure which influences mechanical strength greatly, as well as thermal properties, chemical structure, etc. If it is less than 0.5 % of the total, chemical resistance becomes extremely bad. On the other hand, if it exceeds 20 %, the melt temperature becomes too high and transmission of short wavelengths is remarkably worse.

Alkali metals such as Li_2O, Na_2O, K_2O lower the melting temperature and glass transition temperature. They also increase stability of transmissivity. Therefore, they can be added freely. However, if they exceeds 14 %, chemical resistance is remarkably lowered, and this causes becomes problems in actual use.

Dihydric metal oxides such as MgO, CaO, SrO, BaO, PbO are important components for stability and refractive index. If they are less than 1% or over 60 %, transmissivity becomes unstable.

F lowers the liquid phase temperature of the molten solution and the melting temperature. It can be up to 20 % if necessary. However, if it exceeds this range, achieving uniformity becomes difficult, and high quality optical glass cannot be acquired.

Glass with the range of compositions in the 1st invention above, especially glass where the ratio of P_2O5 is as follows, has relatively high refractive index. It also has optical constants within the range defined by the five points: point A (1.60, 69), point B (1.62, 64), point C (1.62, 47), point D (1.55, 50), and point G (1.56, 73) as shown in figure 1.

P_2O_5	20 to 60 %

Glass with the range of compositions in the 1st invention above, especially glass where the ratio of P_2O_5 and PbO is as follows has relatively high dispersion. It also has optical constants within the range defined by four points: point B (1.62, 64), point C (1.62, 47), point D (1.55, 50), and point E (1.50, 68) as shown in figure 1.

PbO_5	50 to 75 %
PbO	5 to 35 %

It is also possible to add small amounts of SiO_2, Y_2O_3, ZrO_4, As_2O_3, Sb_2O_2 as long as it does not adversely affect the object of this invention or reduce transmissivity, spectral transmissivity , etc.

The optical glass of this invention can be manufactured easily by the following steps. As a starting material, oxides, fluorides, hydroxides, carbonates, nitrates, phosphates of each component element are used. They are weighed and mixed in the desired ratio to make a compound material. This is heated to 1000 to 1300°C, and melted in an electric oven. It is then purified and stirred to make it uniform. Next, it is cast in a preheated metal mold and cooled.

Glass material generally contains high temperature impurities. Among these, Ti, Cr, Ma, Fe, Co, Mi, and Ca are bad. It is necessary to highly refine the starting materials so that the amount of these elements is 5 ppm or less, preferably 3 ppm or less before combining them.

In addition, these elements are prone to enter during the combining or melting process of the starting materials. Therefore, it is necessary to perform these processes in a clean environment. It is necessary to make every effort to limit the amount of these elements: Ti, Cr, Ma, Fe, Co, Ni, and Cu in the glass by taking suitable precautions. If the glass has high amounts of these elements, its transmissivity will be low, especially for UV.

In the following, this invention is going to be explained more specifically according to examples of practice. However, this invention is not limited to only these examples.

(Examples of practice 1 to 30)

Starting material consisting of oxides, fluorides, hydroxides, carbonates, nitrates, and phosphates of each element was prepared. After these materials were refined to a high grade, they were weighed in the ratios stated in table 1 (oxide indication excluding F) and mixed to make a combined material. This was heated to 1,000 to 1,300°C and melted in an electric oven. After refining, stirring, and making it uniform, it was cast in a preheated metal mold . After it was cooled, optical glass was manufactured.

The values in table 1 indicate the component weight ratio in %, and they add up to 100 %.

An elemental analysis was done on the acquired glass □ and the total amount of (indicated in note 1) of Ti, Cr, Mn, Fe, Co, Ni, and Cu was found; and □ refractive index n_d, □ dispersion = Abbe's number ν_d, and □ transmissivity were measured. The wavelengths (nm) where a 10 mm thick glass sample had a transmissivity of at least 80 % is shown in note 2. The smaller the number value, the higher the transmissivity at short wavelengths.

In addition, for comparison, example of practice 3 and 21 were melted without refining the starting materials, and glass was manufactured. The results for these glasses are also shown in table 1.

Table 1

component	Ex of pract 1	Ex of pract 2	Ex of pract 3	Ex of pract 4
Pb_2O_5	72%	71%	71%	70%
Al_2O_3	4	9	9	3
B_2O_3	3	4	5	5
MgO		4	4	
CaO				
SrO				
BaO	16			2
PbO				15
Na_2O	5			5
K_2O		10	11	
F		2		
note1	1.5	1.7	1.0	1.3
n_d	1.53590	1.51341	1.52208	1.55824
ν_d	69.5	71.4	70.7	58.4
note 2	253	242	248	267

Note 1: impurity amount reported in ppm
Note 2: transmissivity is in nm

Table 1 (continued)

component	Ex of pract 5	Ex of pract 6	Ex of pract 7	Ex of pract 8
Pb_2O_5	67%	67%	65%	66%
Al_2O_3	4		3	2
B_2O_3		5		
MgO				
CaO	6	25		3
SrO				
BaO	23			
PbO			29	24
Na_2O			3	
K_2O				5
F		3		
note1	1.2	0.9	1.0	1.3
n_d	1.55725	1.53365	1.58010	1.61201
ν_d	67.8	69.4	50.5	48.2
note 2	252	245	276	270

Note 1: impurity amount reported in ppm
Note 2: transmissivity is in nm

Table 1 (continued)

component	Ex of pract 9	Ex of pract 10	Ex of pract 11	Ex of pract 12
Pb_2O_5	65%	65%	65%	65%
Al_2O_3	4		5	5
B_2O_3		5		
MgO			5	
CaO	10	28	5	10
SrO			20	
BaO	20			20
PbO				
Na_2O		1		
K_2O				
F	1	1		
note1	1.1	0.9	1.2	1.4
n_d	1.55092	1.54712	1.55247	1.55629
ν_d	67.9	68.4	67.3	67.1
note 2	240	243	254	253

Note 1: impurity amount reported in ppm
Note 2: transmissivity is in nm

Table 1 (continued)

component	Ex of pract 13	Ex of pract 14	Ex of pract 15	Ex of pract 16
Pb_2O_5	65%	59%	58%	56%
Al_2O_3	3	3	3	3
B_2O_3	5	4	3	4
MgO				
CaO		8		
SrO				11
BaO	2	26	2	26
PbO	20		30	
Na_2O	5		4	
K_2O				
F				
note1	1.3	0.9	1.2	1.3
n_d	1.56943	1.56340	1.59534	1.57321
ν_d	56.2	66.5	50.6	65.9
note 2	270	254	276	263

Note 1: impurity amount reported in ppm
Note 2: transmissivity is in nm

Table 1 (continued)

component	Ex of pract 17	Ex of pract 18	Ex of pract 19	Ex of pract 20
Pb_2O_5	56%	55%	50%	48%
Al_2O_3	5	5	5	
B_2O_3				10
MgO		10	10	
CaO			9	22
SrO				
BaO	3	28	22	20
PbO	22			
Na_2O	5			
K_2O				
F	9	2	4	
note1	1.0	1.5	1.7	2.0
n_d	1.58216	1.57000	1.56896	1.58585
ν_d	52.2	68.4	69.0	66.8
note 2	285	260	267	275

Note 1: impurity amount reported in ppm
Note 2: transmissivity is in nm

Table 1 (continued)

component	Ex of pract 21	Ex of pract 22	Ex of pract 23	Ex of pract 24
Pb_2O_5	48%	46%	43%	40%
Al_2O_3	3	3	2	2
B_2O_3	9	9	10	6
MgO				
CaO	10	13	10	6
SrO			6	6
BaO	30	29	29	40
PbO				
Na_2O				
K_2O				
F				
note1	1.9	2.0	2.1	2.1
n_d	1.58777	1.58741	1.60300	1.61588
ν_d	67.4	67.5	65.4	63.5
note 2	275	275	275	277

Note 1: impurity amount reported in ppm
Note 2: transmissivity is in nm

Table 1 (continued)

component	Ex of pract 25	Ex of pract 26	Ex of pract 27	Ex of pract 28
Pb_2O_5	36%	34%	29%	27%
Al_2O_3	4	6	6	5
B_2O_3	5			
MgO		3	3	3
CaO	10			
SrO				
BaO	41	48	53	46
PbO				10
Na_2O				
K_2O				
F	4	9	9	9
note1	2.8	3.0	3.2	3.0
n_d	1.60524	1.59046	1.60465	1.61253
v_d	66.6	67.9	67.4	58.9
note 2	276	276	280	280

Note 1: impurity amount reported in ppm
Note 2: transmissivity is in nm

Table 1 (continued)

component	Ex of pract 29	Ex of pract 30	Ex of comp 1	Ex of comp 2
Pb_2O_5	27%	24%	71%	48%
Al_2O_3	5	4	9	3
B_2O_3			5	9
MgO			4	
CaO	8	8		10
SrO		13		
BaO	46	35		30
PbO	5			
Na_2O				
K_2O			11	
F	9	16		
note1	3.0	2.8	10	10
n_d	1.60431	1.56142	1.52208	1.58777
v_d	63.2	72.1	70.7	67.4
note 2	280	272	346	355

Note 1: impurity amount reported in ppm
Note 2: transmissivity is in nm

(Effects of this invention)

As stated above, the optical glass in this invention which has optical constants within the seven ranges shown in figure 1 shows excellent transmissivity at UV wavelengths and also has sufficient chemical resistance for actual use.

Accordingly, this invention expands the potential design and development of optical systems which use UV.

4. Simple explanation of figures

Figure 1 is a plot of refractive index shown by optical glass n4 on the vertical axis and Abbe's number on the horizontal axis. The range defined by seven points of point A (1.60, 69), point B (1.62, 64), point C (1.62, 47), point D (1.55, 50), point E (1.50, 68), point F (1.50, 73), and point G (1.56, 73) defines the range of optical constants suitable for the optical glass of this invention.

Figure 2 is graph of spectral transmissivity. The solid line 1 is that of example of practice 3; the solid line 2 is that of example of practice 21; the broken line 3 is that of example of comparison 1; the broken line 4 is that of example of comparison 2.

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